WETTING KINETICS OF LIQUID ALUMINUM ON AN AL2O3 SURFACE

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Wetting kinetics of liquid aluminium on an Al_2O_3 surface

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The wetting process of a liquid aluminium drop on a solid Al_2O_3 surface has been investigated. Two different models have been proposed: a hydrodynamic model based on the effect of viscosity as well as a diffusion model which considers diffusional effects. The prediction from the models was compared with experiments. It was found that the wetting process of a liquid aluminium drop on an Al_2O_3 surface can be represented by the diffusion model rather than by the hydrodynamic model. In contrast, the hydrodynamic model could be employed to describe the wetting process of a liquid polymer drop on a solid.

1. Introduction

Generally speaking, a study of wetting kinetics is important in the field of engineering applications. For instance in laser-coating technology of a ceramic layer on a metallic substrate, a fast wetting process is required, e.g. of the order of 0.1 s [1], because laser processing itself is a fast process. If the wetting process is slow, the metal–ceramic interface would not be adhered completely before solidification of the materials and the ceramic coating would experience failure after cooling [2]. The spreading of a liquid drop on a solid surface represents a spontaneous wetting process. In fact, it is the most widely employed method to measure the contact angle of a liquid on a solid. However, investigations of wetting kinetics of liquid metal on ceramics are scarce. Laurent *et al.* [3] have measured the variation of contact angle with time in a liquid aluminium drop wetting experiment on Al_2O_3. At 973 K, it takes about 1000 s to reach the equilibrium wetting angle of about 108° in a vacuum of about 5×10^{-4}–5×10^{-5} Pa. With increasing temperature, the wetting time decreases rapidly. However, no accurate measurements (within a short time interval) have been reported at higher temperatures.

The wetting mechanism of liquid metals on ceramics is still under debate. It is known that there exists a thin oxide layer on the surface of liquid metals. This oxide layer has a significant effect on the accurate determination of the equilibrium wetting angle, especially for liquid aluminium [4, 5]. Consequently, the diffusion of metal atoms through the oxide layer around a liquid drop could be important, thereby effecting the wetting kinetics. Similarly, the diffusion of metal atoms on a ceramic surface might also play a role. Therefore, both surface diffusion and diffusion through an oxide layer could affect the wetting kinetics.

In the study of a thin liquid polymer film spreading on a solid surface, a hydrodynamic model of wetting kinetics has been well established [6–9], where the difference of surface tension between the non-equilibrium state and the equilibrium state is treated as the driving force, and the viscosity drag of the liquid film is the resistance to the wetting. However, the wetting kinetics of a liquid drop on a solid surface has not been modelled using a hydrodynamic approach. Some detailed experimental work has been done by Zosel [10]. An empirical formula has been proposed to fit the experimental results [11].

In the present work, two different models for the wetting kinetics of a liquid aluminium drop on Al_2O_3 have been scrutinized: a hydrodynamic model and a diffusion model.

2. Hydrodynamic model

In the hydrodynamic models, the following assumptions have been made: there is no evaporation and absorption of the materials, e.g. the volume of the liquid drop is preserved; there are no chemical reactions or new phases at the interface involved and the wetting takes place at constant temperature, e.g. the surface energy γ_l, γ_s and γ_{ls}, and equilibrium wetting angle, θ_e, are constant during wetting; the solid surface consists of only a single phase and is perfectly smooth, e.g. the hysteresis effect of wetting is neglected.

There are several interactions involved in a wetting process. The difference of surface tension between non-equilibrium and equilibrium states is generally considered to be the major driving forces of wetting. In the case of a liquid drop wetting on a smooth solid surface as represented in Fig. 1, the liquid drop moves in two different directions: both parallel and perpendicular to the solid surface. Because of the effect of surface energy minimum, the liquid drop may retain the shape of a spherical cap if the drop size is relatively small. Thus the radius of the liquid drop is a function of contact angle. The centre of mass of the liquid drop was chosen as a reference position because it is a stationary point for the movement in the x direction; in

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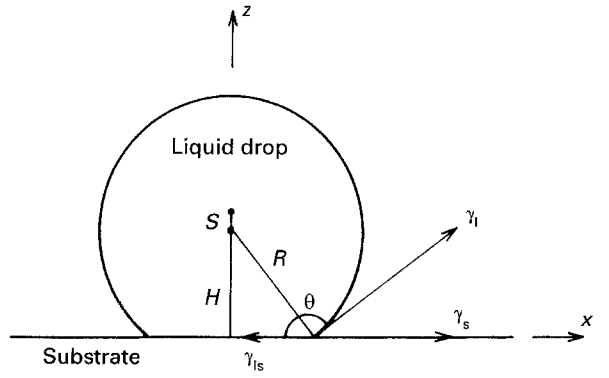

Figure 1 A liquid drop on a solid surface.

the z direction, it represents the movement of the drop. First, we neglect gravity effects, then the difference between surface tensions of non-equilibrium and equilibrium states becomes the only driving force of wetting. Applying the Newtonian equation of fluids to the wetting of the liquid drop on the solid, the following equations can be derived

$$\frac{\gamma_l \cos\theta_e}{2\pi R_e \sin\theta_e} - \frac{\gamma_l \cos\theta}{2\pi R \sin\theta} = \eta \frac{dV_x}{d(S - R\cos\theta)} \quad (1)$$

$$\frac{\gamma_l \sin\theta_e}{2\pi R_e \sin\theta_e} - \frac{\gamma_l \sin\theta}{2\pi R \sin\theta} = -\eta \frac{dV_z}{d(R\sin\theta)} \quad (2)$$

where η is the viscosity of the liquid drop, γ_l is the surface tension of the liquid drop, R is the radius of the drop at a constant angle of θ, and R_e is the drop radius at the equilibrium wetting angle, θ_e. V_x is the velocity of the contact line in the x direction and V_z is the velocity of the mass centre of the liquid drop in the z direction. S is the distance of the centre of mass to the spherical centre of the droplet, and $(S - R\cos\theta)$ represents the distance from the centre to the solid surface. R and S can be expressed as a function of θ.

$$R = R_0\left(\frac{1}{2} - \frac{3}{4}\cos\theta + \frac{1}{4}\cos^3\theta\right)^{-1/3} \quad (3)$$

and

$$S = 2R\cos\left\{\frac{1}{3}\left[\pi + \arccos\left(1 - \frac{R_0^3}{R^3}\right)\right]\right\} \quad (4)$$

where R_0 is the initial radius of a liquid drop at the initial contact angle $\theta_0 = \pi$. According to the geometry illustrated in Fig. 1, the velocity of V_x and V_z may also be expressed as

$$V_x = \frac{d(R\sin\theta)}{dt} = -\frac{R}{2 + \cos\theta}\frac{d\theta_x}{dt} \quad (5)$$

$$V_z = -\frac{d(S - R\cos\theta)}{dt} = -\frac{2R\sin\theta}{(1 - \cos\theta)(2 + \cos\theta)}\frac{(S - R\cos\theta)}{(R + S)}\frac{d\theta_z}{dt} \quad (6)$$

where t denotes the time of wetting. The combination of V_x and V_z contributes to the total wetting process. Therefore, the wetting time, t, can be derived by integrating Equations 5 and 6

$$t = \int_\theta^{\theta_0} \frac{2R\sin\theta}{(2 + \cos\theta)[2V_x\sin\theta + V_z(1 - \cos\theta)(R + S)/(S - R\cos\theta)]} d\theta \quad (7)$$

where the velocities of V_x and V_z can be derived by integration of Equations 1 and 2

$$V_x = \frac{\gamma_l}{\pi\eta}\int_\theta^{\theta_e} \frac{\sin\theta}{(1 - \cos\theta)(2 + \cos\theta)}\left(\frac{S - R\cos\theta}{R + S}\right) \times \left(\frac{1}{\mathrm{tg}\theta} - \frac{R}{R_e \mathrm{tg}\theta_e}\right) d\theta \quad (8)$$

$$V_z = \frac{\gamma_l}{2\pi\eta}\int_\theta^{\theta_e} \frac{1}{2 + \cos\theta}\left(\frac{R}{R_e} - 1\right) d\theta \quad (9)$$

Equation 7 is the basic equation of the hydrodynamic model neglecting gravity effects. It provides the relationship between wetting time, t, and contact angle, θ. In Equations 8 and 9, both V_x and V_z are inversely proportional to $\eta R_0/\gamma_l$ and therefore the wetting time, t, is proportional to $\eta R_0/\gamma_l$. Defining a characteristic time of $t_0 = \eta R_0/\gamma_l$, we obtained a reduced wetting time, $\tau = t/t_0$, which is only a function of contact angle θ and θ_e. If two systems have the same equilibrium angle θ_e, the τ–θ curves will be the same and is called a master curve.

The boundary conditions of Equation 7 are $\theta = \theta_0 = \pi$ at $t = 0$ and $V_x = V_z = 0$, $\theta = \theta_e$ at $t =$ infinity.

During wetting, the surface areas of liquid drop, solid and interface will change, which contribute to the variation of total surface energy during wetting

$$E_\gamma = \gamma_l(S_0 - S_l) - (\gamma_{ls} - \gamma_s)S_{ls} = 4\pi R_0^2\left(1 - \frac{R_0}{R}\right)\gamma_l \quad (10)$$

where γ_l, γ_s and γ_{ls} are the surface tension of liquid, solid and liquid–solid interface, respectively. $S_0 = 4\pi R_0^2$ is the initial surface area of liquid drop, $S_l = 2\pi R^2(1 - \cos\theta)$ the surface area of a liquid drop at a contact angle of θ, $S_{ls} = \pi R^2 \sin^2\theta$ the interface area. The work done by gravity during wetting can be derived as follows

$$E_g = \rho g \Omega \Delta H = \frac{4}{3}\pi R_0^3 \rho g\left(R_0 + R\cos\theta - 2R \times \cos\left\{\frac{1}{3}\left[\pi + \arccos\left(1 - \frac{R_0^3}{R^3}\right)\right]\right\}\right) \quad (11)$$

where ρ is the density of the liquid drop, $g = 9.8\ \mathrm{N\,kg^{-1}}$, $\Omega = (4/3)\pi R_0^3$ is the volume of the liquid drop, $\Delta H = R_0 - (S - R\cos\theta)$ is the displacement of the centre of mass of the liquid drop during wetting. Taking the ratio of work done by gravity to the total work $E = E_g/(E_g + E_\gamma)$, the contribution of gravity to the wetting process can be derived.

Because the velocity, V, is proportional to the square root of energy, we define a gravity function which represents the contribution of gravity to the total velocity: $G = V_g/(V_g + V_\gamma) = E_g^{1/2}/(E_g^{1/2} + E_\gamma^{1/2})$, where V_g and V_γ are the velocities caused by gravity and surface tension. Introducing this gravity function, G, into Equation 7, the following relation t–θ can be

obtained

$$t = \int_{\theta}^{\theta_0} \frac{2R\sin\theta(1-G)}{(2+\cos\theta)[2V_x\sin\theta + V_z(1-\cos\theta)(R+S)/(S-R\cos\theta)]}\,d\theta \quad (12)$$

where V_x and V_z are described by Equations 8 and 9. Obviously the gravity function, G, in Equation 12 depends on the material properties through (ρ, γ) and an initial drop size of R_0. Therefore, if the gravity is operative on wetting, the so-called master curve of τ–θ would not exist.

3. Diffusion model

During wetting, the difference of surface energy between non-equilibrium and equilibrium states contributes to the energy involved in diffusion. The surface energy difference, ΔE_γ, is given by

$$\Delta E_\gamma = \pi r^2\gamma_l(\cos\theta_e - \cos\theta) \quad (13)$$

where r is the radius of the liquid atoms. The thermal vibrations of atoms on a solid surface or in a solid layer are resistant to the wetting process in the diffusion mechanism. According to statistical physics, the probability of an atom jump is given by

$$\nu = \nu_0\exp\left(-\frac{Q}{kT}\right) \quad (14)$$

where ν_0 is the vibrational frequency of atoms, Q is the activation energy of diffusion, k is the Boltzmann constant and T represents the absolute temperature. The net jump of liquid atoms per second which contributes to the wetting is equal to the difference between atoms jumping out of the liquid and atoms jumping into the liquid

$$\Delta\nu = \nu_{out} - \nu_{in} = \nu_0\exp\left(-\frac{Q-\Delta E_\gamma}{kT}\right) - \nu_0\exp\left(-\frac{Q}{kT}\right)$$
$$= \nu_0\exp\left(-\frac{Q}{kT}\right)\left\{\exp\left[\frac{\pi r^2\gamma_l(\cos\theta_e - \cos\theta)}{kT}\right] - 1\right\} \quad (15)$$

Each jump distance is about the atomic distance, i.e. $2r$. Therefore, the moving velocity of the contact line of a liquid drop on a solid surface is equal to the product of $2r$ and $\Delta\nu$. Introducing the frequency factor $D_0 = (2r)^2\nu_0$ into Equation 15, the moving velocity, V_x, can be derived as follows

$$V_x = \frac{D_0}{2r}\exp\left(-\frac{Q}{kT}\right)\left\{\exp\left[\frac{\pi r^2\gamma_l(\cos\theta_e - \cos\theta)}{kT}\right] - 1\right\} \quad (16)$$

According to the geometry of wetting process as sketched in Fig. 1, the moving velocity, V_x, can be also described by Equation 5 in the direction of x. Integrating Equation 5 over θ, then introducing the expression of V_x from Equation 16, the dependence of time on contact angle is

$$t = \int_{\theta}^{\theta_0}\frac{R}{(2+\cos\theta)V_x}\,d\theta = \int_{\theta}^{\theta_0}\frac{R}{(2+\cos\theta)} \times \frac{(2r/D_0)\exp(Q/kT)}{\{\exp[\pi r^2\gamma_l(\cos\theta_e - \cos\theta)/kT] - 1\}}\,d\theta \quad (17)$$

In the case of bulk diffusion or diffusion through an oxide layer, the activation energy, Q, of diffusion includes both the energy of atom migration and the energy of creating a vacancy. But in the case of surface diffusion, Q would only consist of migration energy.

4. Calculations and discussion

4.1. The hydrodynamic model

In order to evaluate the hydrodynamic model, the model was first compared with the experimental results in the case of a liquid polymer drop wetting on a solid surface, as has been investigated systematically by Zosel [10]. Next, the model will be applied to the wetting process of a liquid aluminium drop on an Al_2O_3 surface.

Fig. 2 shows the time–contact angle (t–$\cos\theta$) curves calculated from Equations 7 and 12 including both non-gravity and gravity effects in the case of liquid PIB drop wetting on PTFE. In the calculation, the following material data have been taken from [10]: $\theta_e = 58.5°$, $R_0 = 0.001$ m, $\rho = 1000\,kg\,m^{-3}$, $\gamma = 0.031\,N\,m^{-2}$ and $\eta = 0.03\,N\,s\,m^{-2}$, where the characteristic time $t_0 = 9.67\times10^{-4}$ s. According to Fig. 2, the calculated curve including a gravity contribution fits perfectly with the experimental results, but the curve excluding a gravity effect does not. This suggests that gravity plays an important role in the wetting process.

Fig. 3 illustrates the calculated curves of $t - \cos\theta$ and experimental results for the wetting of a liquid PDMS drop on PTFE with $\theta_e = 28.5°$, $R_0 = 0.001$ m, $\rho = 1000\,kg\,m^{-3}$, $\gamma = 0.021\,N\,m^{-2}$ and $\eta = 0.03\,N\,s\,m^{-2}$ [10]. The characteristic time becomes $t_0 = 1.43\times10^{-3}$ s. The calculated curve including the

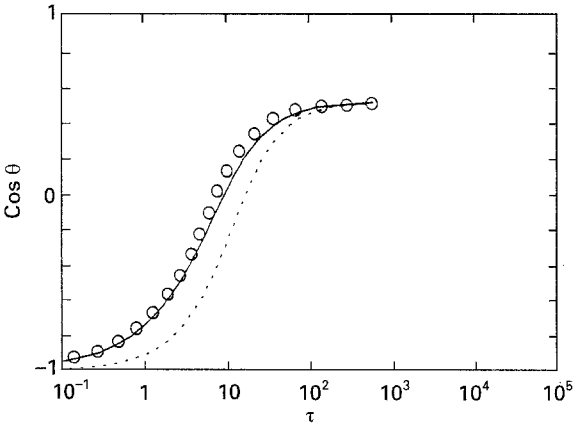

Figure 2 Hydrodynamic model for wetting of a liquid PIB drop on PTFE. τ–$\cos\theta$ curves were calculated from Equations 7 and 12: (——) with gravity effect, (– – –) without gravity effect. (○) Experimental results from [10].

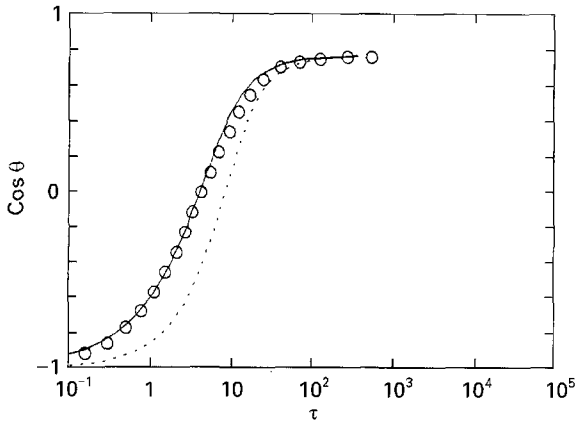

Figure 3 Hydrodynamic model for wetting of a liquid PDMS drop on PTFE. τ–cosθ curves were calculated from Equations 7 and 12: (——) with gravity effect, (– – –) without gravity effect. (○) Experimental results from [10].

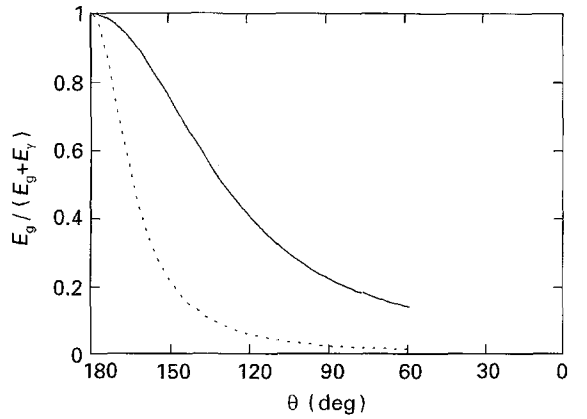

Figure 4 Contribution of the work done by gravity to the total work during wetting. (——) PIM/PTFE, (– – –) Al/Al_2O_3.

gravity contribution also fits rather well with the experimental results.

Fig. 4 depicts the contribution made by gravity to the total work calculated from Equations 10 and 11 for the two systems: a liquid PIB drop on PTFE and a liquid aluminium drop on Al_2O_3. According to Fig. 4, the gravity effect is predominant in the earlier stage of wetting (at higher contact angle θ) and it becomes less important in the latter stage. Gravity is less effective in the wetting of a liquid aluminium drop on an Al_2O_3 than that of a liquid PIB drop on PTFE. This is because the surface tension of liquid aluminium (0.914 $N\,m^{-1}$) is much larger than that of liquid PIB polymer (0.031 $N\,m^{-1}$). Obviously, the gravity effect on the wetting of a liquid drop on a solid surface cannot be neglected, and the hydrodynamic model based on Equation 12 can describe well the wetting kinetics of a liquid polymer drop on a solid surface in contrast to Equation 7.

Now we turn to the hydrodynamic model to study the wetting process of a liquid aluminium on an Al_2O_3 surface. Fig. 5 displays the calculated curves of $t - \cos\theta$ from Equations 7 and 12. The following properties of liquid aluminium wetting on Al_2O_3 at 973 K have been used in the calculation: $\rho = 2700\ kg\,m^{-3}$, $\gamma = 0.914\ N\,m^{-2}$, $\eta = 0.0013$ Ns m^{-2}, $R_0 = 0.001$ m and the equilibrium contact angle $\theta_e = 108°$. According to these data, the characteristic

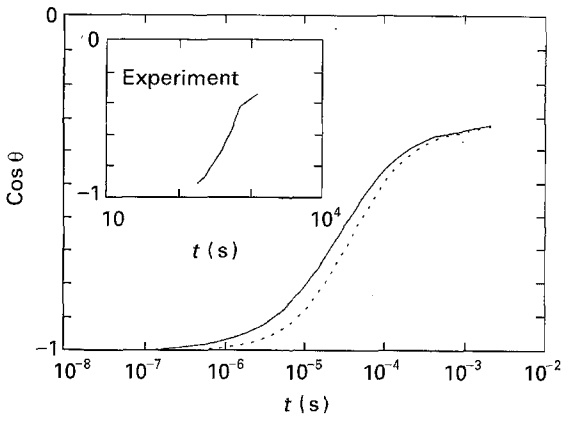

Figure 5 Hydrodynamic model for wetting of a liquid aluminium drop on an Al_2O_3 surface. t–cosθ curves were calculated from Equations 7 and 12: (——) with gravity effect, (– – –) without gravity effect.

time is calculated as $t_0 = 1.422 \times 10^{-6}$ s, which is much smaller than the characteristic time (of the order of 10^{-4} s) of a liquid polymer PIB and PDMS wetting on solid PTFE surface. According to Fig. 5, both calculated curves are in sharp contrast to the experiment results. The actual wetting process turns out to be much slower compared with the prediction from the hydrodynamic model. The results suggest that the resistance from the viscosity flow of the liquid aluminium drop is not the predominant process controlling the wetting kinetics of liquid aluminium on Al_2O_3. It may be concluded that the hydrodynamic model is not applicable to the wetting kinetics of liquid aluminium on Al_2O_3 surface at about 973 K.

4.2. The diffusion model

Equation 17 is the general equation for the diffusion model of wetting kinetics, which is valid for both surface diffusion and diffusion through an oxide layer. First we consider the diffusion process through an oxide layer. Suppose that the oxide layer around a liquid drop is relatively thick, e.g. it behaves like a bulk oxide, then we could adapt some diffusion data from the literature. The frequency factor and activation energy of aluminium in polycrystalline Al_2O_3 have been obtained from Kingery *et al.* [12]: $D_0 = 0.048\ m^2\,s^{-1}$ and $Q = 8.67 \times 10^{-19}\ J\,K^{-1}at^{-1}$. Introducing these data into Equation 17, the time–contact angle (t–cosθ) dependence at 973 K has been calculated and is shown in Fig. 6. In comparison with the experimental results, the calculated wetting time is much too long. Therefore, the assumption of the existence of a thick solid oxide layer around the liquid aluminium drop is not realistic. The oxide layer must be rather thin for the aluminium atoms to diffuse through, and consequently the activation energy, Q, would be smaller.

To the best of our knowledge, there are no diffusion data available for aluminium diffusion on the Al_2O_3 surface. In order to estimate the effect of diffusion on the wetting kinetics, some reasonable diffusion parameters, D_0 and Q, have to be chosen and introduced into Equation 17 to study the behaviour of t–cosθ curves. We choose the same $D_0 = 0.048\ m^2\,s^{-1}$ as

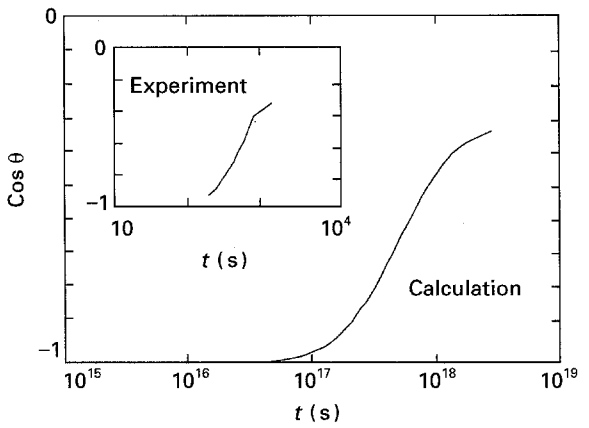

Figure 6 Diffusion model of aluminium atoms diffusion through a thick Al_2O_3 layer. t–cosθ curves were calculated from Equation 17 for wetting of a liquid aluminium drop on an Al_2O_3 surface at 973 K. The experimental results at 973 K are taken from [3].

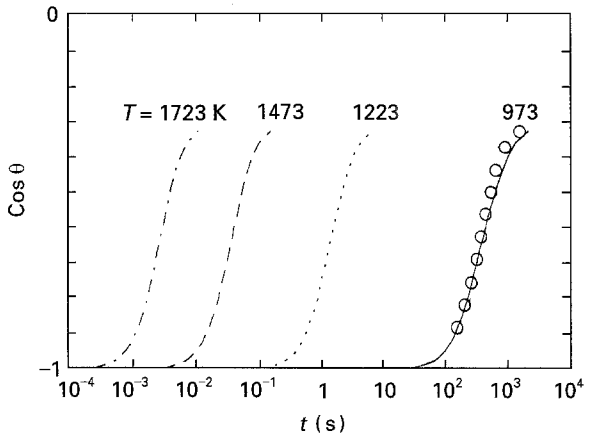

Figure 7 Diffusion model for wetting of a liquid aluminium drop on an Al_2O_3 surface. t–cosθ curves were calculated from Equation 17 at different temperatures for surface diffusion or diffusion through a thin oxide layer. (○) Experimental results at 973 K from [3].

aluminium diffusion in polycrystalline Al_2O_3 and calculated an activation energy in order to fit the experimental results, namely $Q = 4 \times 10^{-19}\,J\,K^{-1}\,at^{-1}$. Introducing these values into Equation 17, several t–cosθ curves at different temepratures have been plotted in Fig. 7. It can be seen that with increasing temperature, the wetting time decreases dramatically. Around 1473 K, the time required for wetting is of the order of 0.1 s. If this prediction is valid, then it would be appropriate to require a fast wetting in some engineering applications, such as in a laser-coating process. An increasing temperature may significantly reduce the wetting time.

It has been suggested that the oxide layer around a liquid aluminium drop will be destroyed at about 1223 K [5]. In this case, the diffusion of aluminium through the Al_2O_3 layer would not be the predominant effect on wetting at high temperature, and surface diffusion would become important.

5. Conclusions

Two different models of wetting kinetics for a liquid drop on a solid surface have been proposed: a hydrodynamic model and a diffusion model. In the diffusion model, the diffusion process of liquid atoms, either on a solid surface or through an oxide layer, is supposed to be the predominant process to the wetting. In the hydrodynamic model, the gravity effect is found to be very important and should not be neglected. The viscosity of the liquid drop is the resistance. In comparison with experimental results, the hydrodynamic model describes well the wetting kinetics of a liquid polymer drop on a solid surface. In contrast it is not suitable to describe the wetting process of a liquid aluminium drop on an Al_2O_3 surface. Here the diffusion process of aluminium atoms on an Al_2O_3 surface or through a thin oxide layer, may be the predominant mechanism of the wetting kinetics.

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